Electrocatalytic reduction of furfural with high selectivity to furfuryl alcohol using AgPd alloy nanoparticles†

John T. Brosnahan, Zhiyong Zhang, Zhouyang Yin and Sen Zhang*  

AgPd alloy nanoparticles were applied for the electrocatalytic reduction of furfural (2-furfuraldehyde). Constant potential electrolysis experiments were carried out and furfural conversions and product selectivities to furfuryl alcohol were systematically investigated to elucidate the alloy composition–catalytic property relationship. AgPd catalysts exhibited faradaic efficiencies to furfuryl alcohol over 95% for Ag60Pd40 at low overpotentials in neutral, aqueous electrolyte.

Increased access to renewable electricity has influenced new technological advances for more sustainable approaches to transform the chemical industry in place today.1 Processes historically powered by fossil fuel combustion are shifting with increasing momentum toward renewability and environmental friendliness. One contributing idea suitable to the green chemistry field is the utilization of non-edible biomass as a feedstock into the existing chemical infrastructure.2 Much industrial interest is associated with three types of biopolymer present in plant cell walls: lignin, cellulose, and hemi-cellulose.3 Hemicellulose is made from branched chains of various sugars including xylose, the majority of which is consumed industrially by up-conversion to yield furfural.4 Furfural is recognized as a platform molecule that can be utilized for the production of a broad variety of value-added chemicals, including furfuryl alcohol, 2-methylfuran, and the dimer product hydrofuroin.5 The current industrial approach to furfural chemistry is thermocatalytic hydrogenation, but electrocatalytic reduction is a promising green alternative.6 Scheme 1 summarizes the production of furfural and common electrochemical reduction products. More than half of industrial furfural is converted into furfuryl alcohol, which is used to make polymeric resins, coatings, and other compounds functioning as fragrances, fuels, and chemical intermediates.7

Due to its existing demand, many thermo- and electrocatalysis studies have targeted furfuryl alcohol, with Pd and Pt having been employed most frequently out of a wide range of precious and nonprecious metal catalysts.8 Although monometallic nanoparticle catalysts have been identified for furfural electro-reduction,9 bimetallic alloying and nanoparticle morphology effects have not been explored in depth. More studies focused on catalyst design and optimization are necessary to advance the implementation of furfural electrocatalytic reduction on an industrial scale.

In this work, we prepared a set of monodisperse AgPd nanoparticle catalysts with controlled bimetallic compositions, and applied them for the electrocatalytic reduction of furfural in neutral, aqueous electrolyte. The Ag was anticipated to promote Pd performance for furfural electrocatalytic reduction, as our previous studies revealed that Pd was subject to over-strong adsorption of aromatic entities and could be effectively modulated by Ag alloying.10 Similar effects have been observed in recent reports where AgPd nanoalloys were used as catalysts in different electrochemical systems.11,12 The results herein demonstrate that bimetallic AgPd alloy nano-

* University of Virginia, Department of Chemistry, Charlottesville, VA 22904, USA. E-mail: sz3t@virginia.edu
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Scheme 1 Summary of furfural production and common electrochemical reduction products derived from furfural.
particles performed with higher furfuryl alcohol selectivity and yield than monometallic Ag and Pd analogues at low overpotentials. Out of the catalysts with varied bimetallic compositions, Ag₆₀Pd₄₀ performed best at −0.4 V and −0.5 V vs. Reversible hydrogen electrode (RHE). We employed this catalyst to further study the effects of electrolytes with different pH. These results suggested that neutral buffer provided an optimal environment for selective furfuryl alcohol production. Competition from the hydrogen evolution reaction (HER) was detrimental to furfuryl alcohol selectivity in acidic electrolytes.

The AgPd alloy nanoparticles were prepared by the co-reduction of Ag and Pd salts in a colloidal synthesis, using our previously reported method \{see ESI Experimental section†\} \(^1\text{3}\) The nanoparticles were loaded onto a carbon support and the catalysts were treated with glacial acetic acid to remove bulky surface ligands for all electrochemical studies, as was also discussed in our previous report. \(^1\text{3}\) We tuned the Ag/Pd atomic composition by controlling the precursor ratio and characterized it using inductively coupled plasma – optical emission spectroscopy (ICP-OES). The calculated metal atom compositions (by atomic percentage) for the nanoparticles used to study alloy effects were Ag₇₅Pd₂₅, Ag₆₀Pd₄₀, Ag₅₀Pd₅₀, and Ag₃₀Pd₇₀. Metal loadings on the electrode surfaces were consistent at 0.6 mg$_{metal}$ cm$^{-2}$ across samples used in each set of experiments.

Fig. 1a-c and Fig. S1† provide transmission electron microscopy (TEM) images of as-synthesized Ag, Pd, and AgPd alloy nanoparticles, and Fig. 1d shows the carbon supported Ag$_{60}$Pd$_{40}$ catalyst after surface ligand removal. These samples are all comparable in size and shape, and the morphologies of the ligand-removed nanoparticle catalysts are uniform. Fig. S2† shows TEM images of Ag, Pd, and Ag$_{60}$Pd$_{40}$ catalysts after use in constant potential electrolysis (CPE) experiments (details in ESI Experimental section† and the discussion below). It indicates that nanoparticle agglomeration is visible under electrochemical conditions for the Ag, but Pd-containing nanoparticle catalysts appear to be more physically stable throughout employment in the system examined here.

Cyclic voltammetry (CV) was employed to create a potential-current profile for the bimetallic and monometallic nanoparticle catalysts, as shown in Fig. S3† Each catalyst displayed an onset of current around 0 V vs. RHE, and the current began to sharply increase for each catalyst around −0.4 V vs. RHE, so we chose to use this as the smallest overpotential in our subsequent CPE studies. Interestingly, the Ag$_{60}$Pd$_{40}$ nanoparticle catalysts exhibits greater current density before the reduction scan reached −0.5 V vs. RHE compared to the pure Ag or Pd counterparts. This suggests that the AgPd alloy nanoparticles should display better catalytic performance than monometallic catalysts at low overpotentials.

Each nanoparticle catalyst was tested for furfural electrocatalytic reduction performance by CPE. Fig. 2 shows the results collected from a typical set of experiments for Ag$_{60}$Pd$_{40}$, which is highlighted here as an example. The ESI† provides detailed equations relevant to our data analysis. Fig. 2a summarizes the furfuryl alcohol yield, carbon balance, and furfural conversion values obtained over six incremental electrolysis experiments from −0.4 V to −0.9 V vs. RHE using Ag$_{60}$Pd$_{40}$. It shows that both the furfural alcohol yield and furfural conversion increase with the use of larger overpotential. Fig. 2b shows the calculated faradaic efficiencies to furfuryl alcohol and H$_2$ for Ag$_{60}$Pd$_{40}$ across the range of potentials. Exceptionally high furfuryl alcohol selectivities are obtained at all these overpotentials, where undesired reactions are not occurring to a significant extent. This catalyst produced furfuryl alcohol with greater than 95% faradaic efficiencies at both −0.4 and −0.5 V vs. RHE. Moving towards more negative potentials, a decrease in the faradaic efficiency to furfuryl alcohol was observed. HER began competing with furfural electrocatalytic reduction around −0.6 V for this catalyst, consuming a larger portion of the current at greater applied potentials. It is worth noting that some other side-reactions might participate at higher electrocatalytic reduction overpotentials, but not enough to elicit product identification and quantification in our study.

The catalytic yields and faradaic efficiencies to furfuryl alcohol using different catalysts were compared in Fig. 3, portraying that each bimetallic alloy material performed objectively better than the monometallic Ag and Pd analogues. Using alloy nanoparticles, HER and undesired side reactions occur negligibly in the conditions studied, and exceedingly high current efficiencies towards furfuryl alcohol are observed. The furfuryl alcohol selectivities reported herein for AgPd nanoparticles are outstanding amongst the existing literature. \(^1\text{4}\) Moreover, plotting the nanoparticle composition against both furfuryl alcohol yield and selectivity reveals a
volcano-type trend at low overpotentials, indicating that an alloy with composition \( \text{Ag}_{60}\text{Pd}_{40} \) is the best selection for this electrochemical reaction condition. Our results suggest that for furfural electrocatalytic reduction, metal alloying is an effective strategy to create more efficient nanoparticle catalysts. This is likely ascribed to the ligand effect and ensemble effect of alloy catalysts, decreasing the affinity of aromatic compounds, and minimizing the poisoning possibility for catalytic sites, as revealed in our previous study of AgPd nanoparticles.\(^{15}\)

Electrocatalytic reduction of furfural may be conducted in a variety of experimental conditions, selection of which will have significant impacts on the chemical process optimization.\(^{16}\) A recent report has indicated that high selectivities to methylfuran and furfuryl alcohol might be obtained depending on the catalyst and electrocatalytic reduction conditions.\(^{17}\) In principle, at low pH, the high availability of protons is beneficial to the formation of metal-hydride species which are coupled to both the 4-electron reduction of furfural to methylfuran, and the 2-electron transfer to produce furfuryl alcohol. Low pH raises issues in furfural electrocatalytic reduction when competing HER limits current selectivity to producing the desired furanic product. To compare the furfural electrocatalytic reduction activity of AgPd in different pH conditions, we performed controlled potential electrolysis analyses in different electrolytes using the most active \( \text{Ag}_{60}\text{Pd}_{40} \) catalyst. The catalyst was tested in four different electrolytes for furfural electrocatalytic reduction: 0.1 M \( \text{H}_2\text{SO}_4 \) (pH 0.95), 0.2 M \( \text{NH}_4\text{Cl} \) (pH 4.9), 0.1 M sodium phosphate buffer (pH 6.8), and 0.1 M potassium phosphate buffer (pH 6.9). Fig. S4† shows pH measurements before and after use in electrocatalytic reduction experiments. Our study has omitted experiments in basic conditions due to a consensus in the literature regarding the instability of furanics at high pH.\(^{16}\) Reliable electrocatalytic product quantification cannot be performed in basic conditions since non-electrocatalytic processes cause chemical changes in the furanic substrate and products.

CVs of the \( \text{Ag}_{60}\text{Pd}_{40} \) catalyst in different electrolytes are provided in Fig. S5†. The CV profile for \( \text{Ag}_{60}\text{Pd}_{40} \) in the presence of furfural in neutral buffer electrolyte displays significantly increased reductive current compared with furfural-free condition, suggesting favorable kinetics for furfural to furfuryl alcohol conversion relative to HER in the neutral condition. This claim is supported by results from the CPE tests in neutral buffer at \(-0.5 \text{ V}\), from which we calculated high and low selectivities to furfuryl alcohol and \( \text{H}_2 \), respectively. Across the range of applied potentials, the measured current density is largest in sulfuric acid electrolyte (pH 0.95), which agrees with other studies detailing the role(s) of protons at the cathode surface during furfural electrocatalytic reduction.\(^{18}\)
AgPd nanoparticles. The neutral buffer electrolyte was found to be the most suitable reaction condition for efficient furfuryl alcohol production due to low furfural reduction overpotentials, along with suppression of HER or other competing processes at neutral pH. This work highlights the crucial role and encouraging potential of alloy nanoparticle catalysts in electrochemical upgrading of biomass-derived platform chemicals.

**Conflicts of interest**

The authors declare no competing financial interests.

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**References**


**Conclusions**

In summary, we studied the bimetallic alloy composition effect on furfural electrocatalytic reduction performance. Ag$_{60}$Pd$_{40}$ nanoparticles were identified with the highest catalytic activity and selectivity for furfuryl alcohol production, superior to Ag and Pd monometallic counterparts and other...